2.5   Zeolites

2.5.1   Introduction

Zeolites are a well-established technology used in a range of processes and industries. Zeolites are not new materials—they have been investigated for over two and a half centuries, with stilbite and natrolite both being identified in the 1750s. Industrial applications include catalysis in the petroleum industry (Venuto and Dekker 1979, Chen et al. 1994), various uses in agriculture (St. Cloud 2007, BRZ Zeolite 2007, Zeolite Australia 2007), horticulture (ZeoPro 2007), gas separations (Yang 1994, Kerry 2007, Kanellopoulos 2000), domestic water treatment (McKetta 1999, Kawamura 2000, Faust 1998); and nuclear waste processing (Auerback et al. 2003, Choppin and Khankhasayev 1999). The value of zeolite catalysis to petroleum cracking is well in excess of $200 billion (MassNanoTech 2007). About 50 naturally occurring zeolites have been identified; over 150 synthetic zeolites have been prepared and characterized; and further thousands of combinations of framework and composition are available (MassNanoTech 2007, Baerlocher and McCusker 1996). Zeolites have long been used in the nuclear industry (Auerback et al. 2003, Choppin and Khankhasayev 1999) owing to their properties as ion exchangers. The planned siting of the United States' first deep geologic radioactive waste repository at Yucca Mountain in Nevada, where design philosophy called for both engineered and natural barriers (Ahn et al. 1981) to inhibit the transport of any potentially leaking radionuclides, was influenced considerably by the local abundance of the natural zeolites mordenite and clinoptilolite, both of which have large cationic exchange capacities.

2.5.2   Description

Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional nano- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of $[SiO_4]^-$ and $[AlO_4]^-$ tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1-2 nm diameter running through the material. Figure 12 shows a representation of a typical zeolite framework. It should be clearly noted that this is just one of a large and growing number of types of zeolite framework. In 1970, the Atlas of Zeolite Framework Types (Baerlocher and McCusker 1996) listed 27 known frameworks, but by 2003, the number had grown to 145. The variety of size and shape available for the pore structure is the source of zeolites' catalytic activity that is so important to the petrochemical industry.

A second consequence of the framework being built from negatively charged units is that it possesses a net negative charge that must be balanced by the presence of positively charged cations. Most naturally occurring zeolites have the environmentally predominant sodium ion as a loosely bound counter ion. These can be readily displaced by other ions for which a particular framework has a much greater affinity, thus giving zeolites significant ion exchange properties.
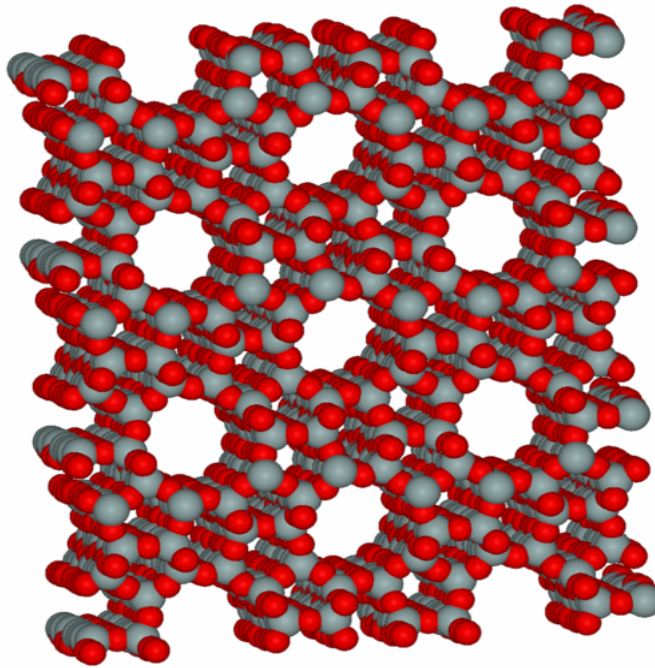
Figure 12. A typical zeolite structure

It should be noted that the ion exchange and the pore size properties of zeolites are partially linked. When the zeolite is in the sodium form (i.e., it has positively charged sodium ions balancing the net negative charge on the aluminosilicate framework), the sodium ions are associated with the tetrahedral aluminum or silicon atoms at the entrance to the pores and, because of their finite size, they effectively reduce the diameter of the pore opening slightly. If the sodium ions are replaced by potassium ions, which are larger than the sodium ions, then the opening of the pore is effectively reduced even further. This behavior permits a degree of control over the size of material that can enter the pores.

Zeolites are usually aluminosilicates, but other tetrahedral atoms such as phosphorus, gallium, germanium, boron, and beryllium can exist in the framework as well.

2.5.3 Potential Applications

General Applications. Zeolites have a wide range of commercial uses (InterSun 2007), including:

Aquaculture
- Ammonia filtration in fish hatcheries
- Biofilter media

Agriculture
- Odor control
- Confined animal environmental control
- Livestock feed additives

Horticulture
- Nurseries, greenhouses
- Floriculture
- Vegetables/herbs
- Foliage
- Tree and shrub transplanting
- Turf grass soil amendment
- Reclamation, revegetation, and landscaping
- Silviculture (forestry, tree plantations)
- Medium for hydroponic growing

Household Products
- Household odor control
- Pet odor control

Industrial Products
- Absorbents for oil and spills
- Gas separations

Environmental Applications. Although environmental applications of zeolites are small compared with applications of their catalytic properties, considerable research and some implementations have taken place including:

Radioactive Waste
- Site remediation/decontamination

Water Treatment
- Water filtration
- Heavy metal removal
- Swimming pools

Wastewater Treatment
- Ammonia removal in municipal sludge/wastewater
- Heavy metal removal
- Septic leach fields

Pasini (Pasini 1996) has described the state-of-the-art technology with regard to the use of natural zeolites in the protection of the environment. He focuses on the possible cation exchange procedures and principles that can be operated at an industrial level; the removal of NH_4^+ from municipal and industrial wastewater; the possibilities for use of natural zeolites for removal of heavy metals from water after laboratory experiments; and how chemical and structural features make zeolites a powerful tool for the decontamination of waters containing radionuclides. The compendium by Misaelides et al. (1999) dealt with general environmental applications and contained much information on the use of zeolites as radionuclide sorbents (Macasek 1999, Bish 1999, Rajec et al. 1999, Colella 1999), including consideration of the sorption and leaching properties of the composites and complexes of natural microporous materials; investigation of natural zeolites and nuclear waste management in the case of Yucca Mountain, Nevada; the sorption of heavy metals and radionuclides on zeolites and clays; and environmental

applications of natural zeolitic materials based on their ion exchange properties. As an example of the depth to which these studies can go, Komarneni (Komarneni 1985) investigated the use of one zeolite, phillipsite, in cesium decontamination and immobilization, citing:

> *"The use of zeolites such as clinoptilolite in nuclear waste decontamination is a common practice (IAEA 1972). Zeolites and zeolitic tufts have also been used to decontaminate low and intermediate-level liquid nuclear wastes (Mercer and Ames 1978) and to separate 37Cs from high-level radioactive defense wastes at Hanford, Washington (Nelson and Mercer 1963, Brandt 1970, Buckingham 1970). Zeolitic ion ex-changers, such as Ionsiv IE-95 (USNRC 1980) which consists of a mixture of natural chabazite and erionite from Bowie, Arizona and Ionsiv IE-96 (which consists of chabazite) + Linde A-51 (Hofstetter and Hitz 1983) are currently used to clean up accident wastewater at the Three Mile Island-Unit II reactor, Middletown, Pennsylvania."*

Radionuclide Applications. Zeolites are one of the few nanotechnologies that have been investigated for environmental remediation purposes. Because of their ion exchange properties, and the fact that they are a seemingly benign natural product that can bring certain improvements (such as increasing the soil cation-exchange capacity and soil moisture, improving hydraulic conductivity, increasing yields in acidified soils, and reducing plant uptake of metal contaminants) to soil properties (Allen and Ming 1995), zeolites have been examined for their ability to remediate heavy metals in soil (Weber et al. 1984). Based on this work, Campbell and Davies (Campbell and Davies 1997) performed an experimental investigation of plant uptake of cesium from soils amended with clinoptilolite and calcium carbonate.

The origin of this work was the observation that radioactive cesium (^{137}Cs) from the Chernobyl accident of 1986 has unexpectedly remained in a bioavailable form in upland, sheep-grazing soils of Great Britain. As a potential remedial measure, the zeolite clinoptilolite was tested in a greenhouse pot experiment for its effectiveness in selectively taking up cesium from two British soils: a lowland loam and an upland peat. Rye-grass grown on 10% clinoptilolite-treated soils resulted in grass leaf tissue cesium concentrations below 30 mg Cs kg^{-1} grass in all cases. Where no clinoptilolite had been added, cesium in grass leaf-tissue reached 1,860 mg kg^{-1} in rye grown on peat and 150 mg kg^{-1} in rye grown on loam. In contrast, the addition of calcium carbonate to the Cs-treated, clinoptilolite-free peat soil enhanced the grass concentration of Cs by approximately five times, but this effect was not observed with the concentration of Cs in grass grown from loam soils with the same treatments.

However, despite this apparent beneficial result of adding the zeolite, adverse side effects were observed. Since the zeolite is in the sodium form, sodium ions are released and the risk of sodium toxicity to plants increases as cation exchange proceeds. Further, since clinoptilolite binds heavy metals in general, essential heavy metals (such as zinc) would be markedly decreased by the application of zeolite, which in turn could result in deficiency problems in animals. It was also noted that since grazing animals consume a

considerable amount of soil in their diet, the consumption of radionuclide-laden zeolites could itself bring risks.

In general, it has been noted that the main research behind the use of natural zeolites as a remediation tool for contaminated soil has been conducted largely through laboratory and greenhouse trials. There is very little evidence in the literature to support the long-term use of natural zeolites in real remediation projects (Stead et al. 2000). It was also noted that the future potential of using zeolites has not been fully appreciated, and that there is an urgent need to undertake field trials and evaluate the in-situ efficiency for these remediation purposes.

Since zeolites are natural materials and are mainly used in industrial processes, little research is focused on their fate and transport, though an extensive volume of work exists on their geological origin and behavior. Extensive data exists on operation and maintenance parameters. As would be expected, specific details are highly dependent on waste streams involved. Three references (IAEA 1967, IAEA 1984, IAEA 2002) discussed below provide an excellent overview of the issues involved.

2.5.4 Impacts, Hazards, Efficacy, and Limitations

Zeolites are a bulk commodity. World production is on the order of 4 million tons per year, with China producing and using about 2.5 million tons (primarily as a low-grade additive to pozzolan cement); U.S. consumption is about 0.5 million tons. The primary industrial use is as a petrochemical catalyst and the second largest use is as a detergent builder. Thus, the use of zeolites in radionuclide remediation would be expected to have little impact. Most zeolites, particularly those with current widespread uses, are regarded as a safe material; they are currently being marketed as a health food and references to their medicinal use date back thousands of years. Zeolites are also used as a feed additive for cattle, pigs, chicken, and fish. It should be noted, however, that one zeolite, erionite, is regarded as a carcinogen due to its fibrous nature and high iron content.

Regarding efficacy, though zeolites have had limited uses in environmental remediation outside of their use in the nuclear industry as an ion exchanger for liquid radioactive waste management, they are seen as having significant potential. Even the drawbacks mentioned in the work of Campbell and Davies (Campbell and Davies 1997) (discussed in Section 2.5.3) should be surmountable. To eliminate the sodium toxicity risk to soil, the zeolite could be preconditioned into the ammonium form, which would likely lead to plant growth improvements. Overcoming the concern of nutritionally important soil nutrients binding together would require that the zeolite used (possibly synthetic) would be designed to have a very high specificity for the target radionuclide and little else. Alternatively, soil quality could easily be monitored and appropriate amendments made.

2.5.5 Management of Zeolite Wastes

Ion exchange in general is one of the most well-developed, common, and effective treatment methods for liquid radioactive waste, and is widely used in the nuclear industry. Zeolites are a large component of the inorganic ion exchangers used and an

extensive amount of literature exists on various aspects of their treatment and disposal. Among the best overviews of this technology base are the series of technical reports issued by the International Atomic Energy Agency (IAEA) in 1967, 1984 and 2002 (IAEA 1967, IAEA 1984, IAEA 2002). The information below draws largely from the most recent of these reports (IAEA 2002).

Prior to treatment for disposal, two pre-treatments—dewatering and size reduction—may be needed. Dewatering is generally accomplished by pressure, vacuum filtration, or centrifugation. If drying is needed, hot air is usually used as the drying medium with a shallow bed of spent materials. Types of drying units include fluidized bed dryers, vertical thin film dryers, and cone dryers.

Since inorganic ion exchange materials (such as zeolites) are generally resistant to degradation by radiation or biological actions, they are treated by the use of direct immobilization, or by high temperature processes (such as vitrification). The immobilization matrices currently used include vitrification, cement, bitumen encapsulation, polymer encapsulation, and disposal in high-integrity containers.

Vitrification has been widely evaluated for the immobilization of highly-active waste, such as waste from the reprocessing of spent nuclear fuel, and has been evaluated for the treatment of ion exchange resins (Jantzen et al. 1995, Cicero-Herman et al. 1998). The excellent leach resistance property of the resulting glass waste form is the principal advantage of vitrification. Vitrification processes are capital-intensive, and the melters have a relatively short operational life (approximately 5 years). Vitrification processes operate at temperatures ranging from 1100°C to 3000°C, depending on the waste composition and glass forming additives used.

Cement immobilizing radioactive waste has been used in the nuclear industry and at nuclear research centers for more than 40 years. Detailed descriptions of the process can be found in references from the IAEA in 1993 and the Los Alamos National Laboratory in 1997. Cement has many characteristics in its favor: it is readily available and widely used in civil engineering, the raw material is inexpensive, and the processing equipment can be based on conventional technology. The resulting waste forms are strong; noncombustible and radiation resistant, have a high density (providing radiation shielding), have a reasonable chemical stability, and have a moderate resistance to the release of radionuclides. The high pH conditions typical for cement results in a low solubility for many radionuclides by the formation of hydrolyzed species, carbonates, etc., which provides a good resistance to leaching. The main disadvantage of the cementation of spent ion exchange materials is that the final waste volume is high compared with the initial volume, owing to the low waste loadings that are achievable. The loadings can be increased by a pretreatment (such as grinding) of the spent ion exchange materials before cementation, which improves the quality of the final cemented products.

Bitumen is a generic term used to cover a wide range of high molecular weight Hydrocarbons. Bitumen encapsulation is currently not used in the United States for

disposal, although several bitumen varieties are commercially available overseas for the immobilization of radioactive waste, including spent ion exchange resins. The main characteristics that make bitumen suitable as a matrix material are:

- Its insolubility in water;
- Its high resistance to the diffusion of water;
- Its chemical inertness;
- Its plasticity and good rheological properties;
- Its good aging characteristics;
- Its high incorporation capacity, which leads to high volume reduction factors; and
- Its instant availability at a reasonable cost.

However, since it is an organic material, bitumen has the following disadvantages:

- It decreases in viscosity as a function of temperature, leading to a softening of the matrix, which melts at temperatures of about 70°C;
- It is combustible, although not easily flammable (the flash point and flammability temperatures are higher than 290°C to 350°C, depending on the type of bitumen);
- It has a lower stability against radiation than cement, especially under the higher radiation fields often associated with spent ion exchange media; and
- It reacts with oxidizing materials such as sodium nitrate.

The immobilization of spent ion exchange resins in polymers is practiced at many installations worldwide. Different types of polymers are used and further studies to improve cost effectiveness, process simplicity, and product quality are being carried out in many countries. Among the many polymers used are epoxy resins, polyesters, polyethylene, polystyrene and copolymers, urea formaldehyde, polyurethane, phenol-formaldehyde, and polystyrene.

2.5.6 Summary of Environmental Potential

Zeolites are a well-established technology with a variety of industrial uses ranging from construction materials and detergent builders, to catalysts and separation agents. They are one of the oldest separation technologies for the removal of radioactive components from aqueous waste streams. The flexible tectonic structure and ability to be chemically "tailored" to specific target species continues to stimulate their development. In addition to their use as an "end-of-pipe" treatment for aqueous streams, zeolites are one of the few materials offering the possibility of being an inexpensive amendment to soils contaminated with radioactive species, since extremely high species selectivity and binding strength can be designed into the material. Continued investigation of zeolites in general is expected due to their catalytic properties; research in this area should support further developments, potentially leading to environmental applications.

2.5.7 References

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2.6   Other Nanoparticles

Though iron nanoparticles presented in Section 2.2 are the most fully developed type of nanoparticle for environmental remediation, they are not the only type of nanoparticle that has been suggested for environmental remediation. Some additional possibilities include the use of TiO_2 nanoparticles as photocatalysts for the destruction of organic pollutants (Rajh et al. 2003), the separation of ionic solutes using nanoparticle-crosslinked polymer hydrogels (Thomas et al. 2003), or the use of coated magnetic nanoparticles in high-gradient magnetic separations (Moeser et al. 2004). The subsections below present information on three possibilities: nanodiamonds, dendrimers, and Argonne Supergel.

Nanodiamonds are the subject of much research due to their potential in electronic and bio-imaging applications, and because they can be prepared directly, simply, and in potentially large amounts. They are apparently biologically benign, and their ease of surface functionalization and magnetic properties make them a potential separation platform.

Dendrimers are a new class of polymer with tailorable properties, both at the surface and in the interior of the particle. They have been of great interest in the area of separations, and are potential complements to separation processes involving nanofiltration or microfiltration.

Argonne Supergel is presented as a nano-enabled technology developed specifically for radionuclide decontamination. These three examples (nanodiamonds, dendrimers, and Supergel) are presented to provide a sense of the range of possibilities that nanoparticles can offer for separation-based remediation.
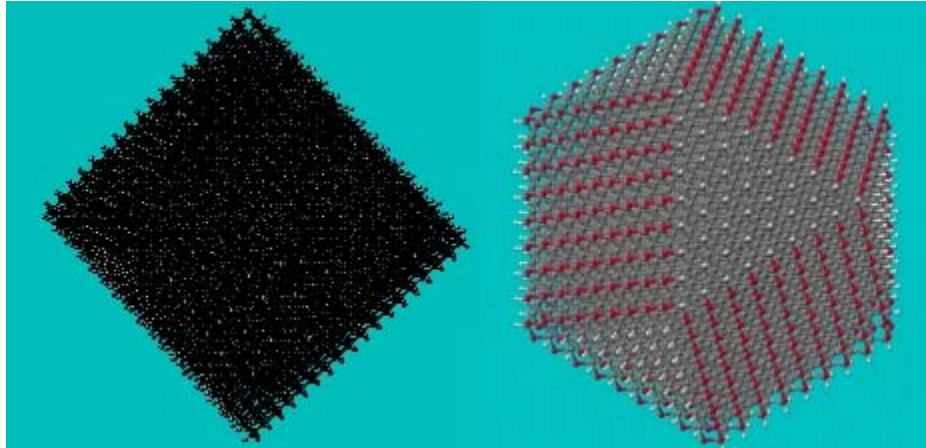
2.6.1 Nanodiamonds

Nanodiamond is a term used for a group of diamond-related materials with nanoscale dimensions, including diamond films and diamond nanoparticles. These are prepared by a variety of methods, including high-pressure gas-phase nucleation and application of shock waves to graphite (Dolmatov 2001). Within this group of diamond materials lies a subgroup called detonation Nanodiamond (DND), or ultrananocrystalline diamond (UNCD). These materials were discovered in Russia in 1963, and produced by the detonation of oxygen deficient explosives, such as a 3-to-2 mixture of 2,4,6-Trinitrotoluene (TNT) and Hexahydro-Trinitro-Triazine (RDX). Figure 13 shows a Transmission Electron Microscope (TEM) image of DNDs.

DNDs were unknown in the West until recently, and have attracted much interest (Petrov et al. 2006, Gruen et al. 2005) because of their unusually uniform shape and size distribution and the fact that they can be produced in large quantities (Osawa 2003). Before DND was widely known, Western industry produced microdiamonds by applying an externally produced shockwave to heated graphite at high pressures. This produced a polycrystalline material with a wide size distribution and very few particles reaching

down to the 10-20 nm size range. In contrast, DND has a fairly tight size distribution in the 3-5 nm range, consisting of about 5,000 carbon atoms, and has a regular octahedral shape (Figure 14).
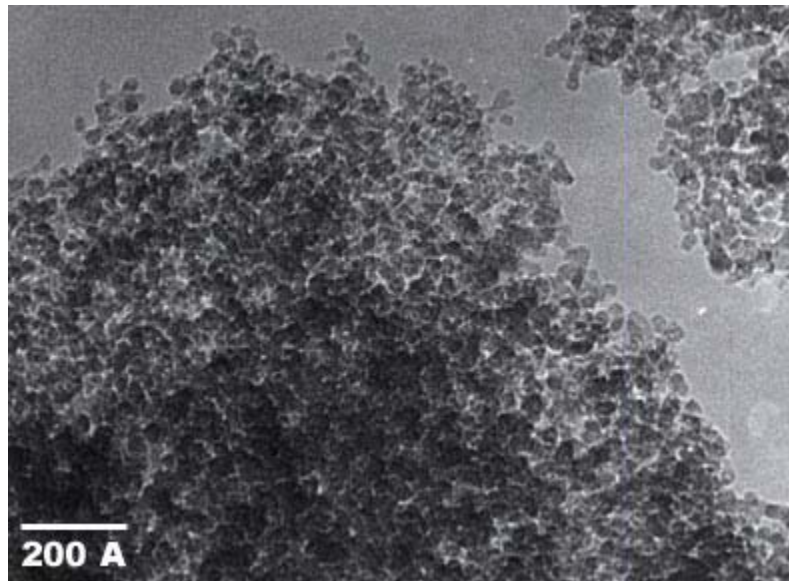

Figure 13. TEM image of DND

Figure 14. Model of nanodiamonds demonstrating their regular octahedral shape

Nanodiamond production from a detonation produces a sooty product that is approximately 50% DND. To obtain the nanodiamonds from this mixture, two challenges must be overcome—the presence of graphitic impurities and the fact that the diamonds tend to aggregate into clusters with average sizes of 30 μm, 3 μm, and 100-200 nm. The aggregates can be broken up by a combination of ultrasound and high-speed zirconia bead milling.

Nanodiamonds possess interesting properties. Their surfaces have a tendency to change from the regular diamond structure to a fullerene (buckyball) structure (Figure 15), resulting in a material that appears to have a diamond within a fullerene cage and has some of the physical properties of the nanodiamond combined with the rich chemistry of the fullerene.
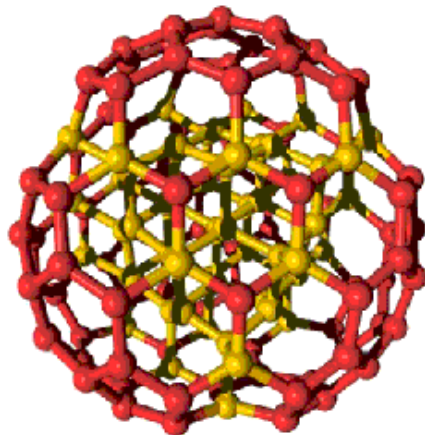
Figure 15. Structure with nanodiamond center and fullerene-like surface

The potential for surface chemical functionalization opens up a wide range of possible applications for derivatized material. Even without chemical functionalization, nanodiamonds have been suggested for a range of applications, including:

- Lapping and polishing applications
- All-rigid memory disk substrate
- Polycarbonate and CR-39 eyeglass lenses
- Miniature and precision ball bearings
- Optical and laser optical components
- Ceramics
- Precious stones
- Metallic mirrors and precision metal polishing
- Ferrite surface preparation
- Mechanical seal lapping
- Superhard and soft nanoabrasives

Other applications include:

- Surface germination for following growth of diamond-like films
- Ni-Diamond and Cr-Diamond electroplated hard coatings
- Molecular sieves
- Lubricant additive to engine oil
- Dry lubricants for metal industry (drawing of W-, Mo-, V-, Rh-wires)
- Reinforcing fillers for plastics and rubbers
- Chromatographic carriers

A major area that is being investigated is the biomedical potential of nanodiamonds, including their roles as drug carriers, implant coatings, and medical nanorobots. Nanodiamonds are soluble in water, can be functionalized, and appear to be biologically benign. Cytotoxicity research findings from the University of Dayton indicate that nanodiamonds are biologically compatible materials across a range of sizes with regard to a variety of cell types, with or without surface modifications (Schrand et al. 2007).

Nanodiamonds have also been suggested as sorbent materials (Dolmatov 2001, Gruen et al. 2005), giving rise to the possibility of environmental remediation applications. Their observed magnetic properties (Talapatra 2005) also open the possibility of their use in magnetic separations. The radiation stability of the carbon also opens up the possibility as a disposal waste form.

2.6.2 Dendrimers

A dendrimer is a highly and repetitively branched, three-dimensional polymer created by a sequence of iterative chemical reactions starting from a central core. Each iteration is known as a generation and has twice the complexity of the prior generation. The term comes from *dendron* (the Greek word for tree), with the analogy being the branch-like structure of the dendrimer. Dendrimers have been called the fourth major class of polymeric architecture (after linear, cross-linked, and branched polymers), but unlike other polymers where atom-by-atom control is not feasible and polydispersity (and the variability it brings) is an inherent characteristic, dendrimers are characterized by monodispersity (i.e., all dendrimer molecules are of a uniform and controllable size) and well-defined properties. Figure 16 provides a graphical representation of a generalized dendrimer structure.
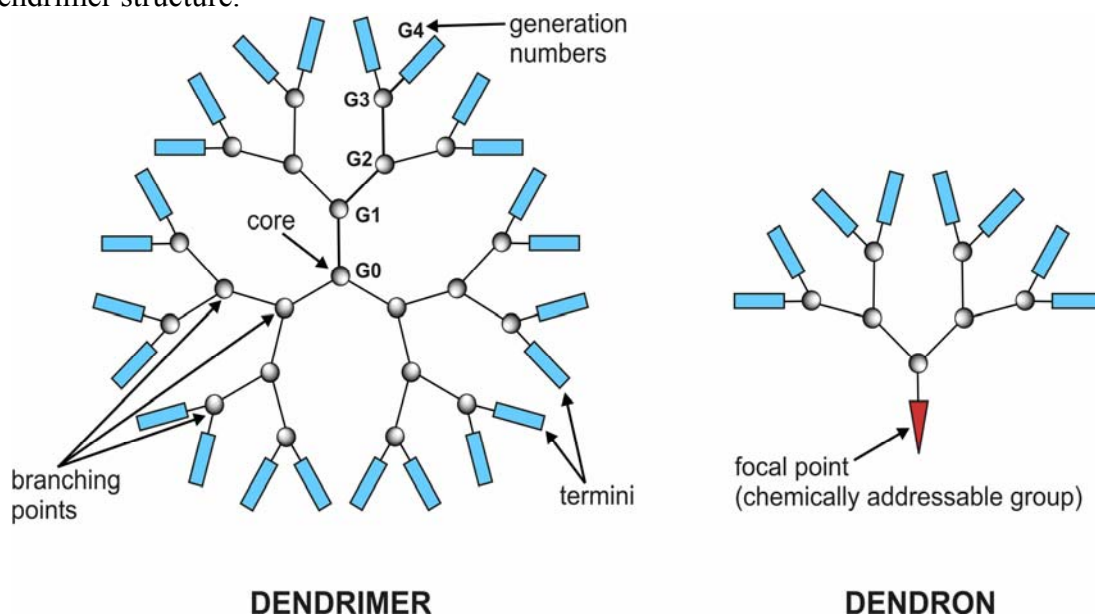
Figure 16. A generalized dendrimer structure

Figure 16 allows some of the special chemical properties of dendrimers to be explained. Starting at the core (G0) and moving through branching points G1 and G2, it can be seen that as the dendrimer branches out in a predictable manner, large voids can exist within the dendrimer internal structure. Both the size and the physical nature (e.g., hydrophobic or hydrophilic characteristics) of these voids can be controlled during synthesis by judicious selection of both the length and composition of the branch backbone. These voids can be used to store material (metals, organic and inorganic molecules, and even other nanoparticles), and together with the fact that dendrimers can easily move across biological membranes, the controllable nature of the voids has led to suggested applications of dendrimers as carriers of genetic material into cells (Kukowska-Latallo et al. 1996), drug delivery agents (Lim and Simanek 2005), and diagnostic imaging agents (Tomalia 2003). The voids can also be used to hold material undergoing reactions and has led to investigations of dendrimers as nanoreactors (Chung and Rhee 2003).

A second feature that is illustrated in Figure 16 is the surface formed by the terminal groups. As the number of generations of the dendrimer increases, the total external surface area rises dramatically. If the terminal groups are designed to be binding moieties for other species, then it is apparent that a dendrimer, compared to say a macroscopic bead of ion exchange resin (which will have a much smaller surface area than an equivalent amount of dendrimer), can potentially bind up a large amount of target material. It is this aspect of dendrimers that is of prime concern for environmental applications. Current expertise in dendrimer synthesis also allows for more than one type of terminal group to be attached to the dendrimer, thus offering the possibility of multifunctional molecules. Terminal groups can be attached to modify solubility, modify binding capacity and specificity, and to allow further reaction with or attachment to other surfaces or nanoparticles. It has been suggested that amphipathic dendrimers could be synthesized with one half of the molecule (or one hemisphere) covered in hydrophobic groups, and the other half containing hydrophilic groups.

Due to the degree of structural control that dendrimers make possible, and the fact that their highly customizable properties should make them building blocks for other nanomaterials, they have been the subject of much research, with the number of academic publications approaching ten thousand. Commercial development has been slower than once anticipated because of their high cost (on the order of $10 per milligram) and the complexity of scaling-up production. Though these factors are themselves subject of much research, dendrimers already have a market or near-market presence:

- Dade Behring, one of the world's largest medical diagnostic firms, is developing a dendrimer-based, rapidly responding tool for detecting heart attacks and cardiac damage.
- The U.S. Army Research Laboratory is developing a dendrimer-based anthrax detection agent.
- Starpharma is developing the world's first dendrimer-based drug, Vivagel, to fight sexually transmitted infections. It has been awarded $20 million by the National Institutes of Health (NIH) to develop its HIV indication; given further awards to

develop its genital herpes indication; and was granted Fast Track status by the U.S. FDA in 2006 as a product for preventing HIV infection.

Dendrimers are currently under investigation as metal sequestering agents for waste remediation technologies (Cohen et al. 2001), and for the removal of uranium from aqueous streams (Diallo 2007). In the latter work, dendrimers may be compared with chelating agents, which are widely used in uranium separation processes, such as solvent extraction or ion exchange resins. Ion exchange resins with amino groups typically bind on the order of 100 mg of uranium per gram of resin, while the work with poly(amidoamine) and poly(propyleneimime) dendrimers, which contain nitrogen and oxygen donors, can bind up to 2500 mg of uranium per gram of dendrimer without reaching saturation in either acid or basic solutions. Further, the binding kinetics of the dendrimers to uranium is very fast and reaches equilibrium in less than 20 minutes. Rapid equilibration, high loading capacity, and selectivity mean that such dendrimers could thus serve as high capacity and selective chelating agents for uranium. The dendrimer-uranium complexes could be easily separated by ultrafiltration and then regenerated, thus avoiding the need to add further reagents and simplifying the overall process.

2.6.3 Argonne Supergel

Argonne National Laboratory (ANL) has developed a system, called the "Supergel" technique, to safely capture and dispose of radioactive elements in porous structures outdoors (such as buildings and monuments), using a spray-on, super-absorbent gel and engineered nanoparticles (ANL 2006). Porous structures are notoriously hard to clean. In decommissioning and decontamination operations, it is common practice to demolish contaminated structures or completely remove a significant surface layer rather than attempt to remove radioactivity. ANL's Supergel technique preserves surfaces, which means that monuments or buildings would not have to be defaced to remove radiation. The Supergel was developed with funding from the Department of Homeland Security to help fill a technology gap in preparedness for a terrorist attack with a "dirty bomb" or other radioactive dispersal device, but it could also be used in more general decontamination situations.

The Supergel technique uses commercially available equipment in a simple procedure. First, a wetting agent and a super-absorbent gel are sprayed onto the contaminated surface. The polymer gel used to absorb the radioactivity is similar to the absorbent material found in disposable diapers. When exposed to water, the polymers form something similar to a structural scaffold that allows the gel to absorb a large amount of liquid. When sprayed on concrete, the wetting agent causes the bound radioactivity to re-suspend in the concrete pores and the superabsorbent polymer gel then draws the liquid out, along with the resuspended radioactivity. Inside the gel, the radioactive material becomes fixed by engineered nanoparticles that also reside in the gel. After a period of standing, the gel is vacuumed and recycled, leaving behind a relatively small amount of radioactive waste for disposal.

2.6.4 Summary of Environmental Potential

These three technologies—nanodiamonds, dendrimers, and Supergel—demonstrate the broad potential of nanoparticles. Nanodiamonds, though relatively new, offer a wide range of potential applications and can be produced in bulk at reasonable prices. Dendrimers are a new class of polymer architecture that has caused much excitement due to the potential of engineering properties at the molecular level into materials of uniform and controllable size. The Argonne Supergel shows the ease with which nanoparticles can be incorporated into other applications to address highly specific technology needs.

2.6.5 References

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2.7   Uranium Reduction by Bacteria

Bioreductive immobilization of uranium is a quasi nanotechnology. The precipitated uranium and other minerals are in the form of nano size particles, whereas the bacteria are about 1 μm. In this section, the process is described, equations are provided, and photographs presented showing the nanoscale uraninite particles.

The large number of contaminated sites and volumes of contaminated groundwater and soil call for innovative and economically attractive remediation technologies. To date, pump-and-treat is the most widely used technology. Frequently, pump-and-treat has been ineffective in permanently lowering contaminant concentrations in groundwater (Travis and Doty 1990). A recent study by Quinton et al. (Quinton et al. 1997) showed that groundwater cleanup technologies (such as pump and treat, permeable reactive barriers with ZVI, and bio-barriers) are more expensive than in-situ bioremediation.

Microorganisms can reduce uranium indirectly by producing hydrogen sulfide (H_2S) or pure hydrogen (H_2) in the course of other processes (abiotic reduction) or directly using enzymes (enzymatic reduction). The first microorganisms identified to enzymatically reduce U(VI) were the dissimilatory Fe(III)-reducing microorganisms, *Geobacter metallireducens* and *Shewanella putrefaciens* (Lovley et al. 1991). These microorganisms used uranium as an electron acceptor, H_2 or acetate as an electron donor to support growth, and tolerated U(VI) concentrations as high as 8 mM. Several authors studied the enzymatic reduction of U(VI) by various pure or mixed cultures of microorganisms, including metal- and sulfate-reducing bacteria (a summary of previous work can be found in Abdelouas et al. 1999a). These authors reviewed the literature on microbial reduction of uranium and the significance of biogeochemical processes related to uranium mining, tailings, and groundwater remediation. In Figure 17, the key reductive and oxidative reactions are shown for this process; in Figure 18, a bacterium is shown surrounded by nanosize uraninite particles.
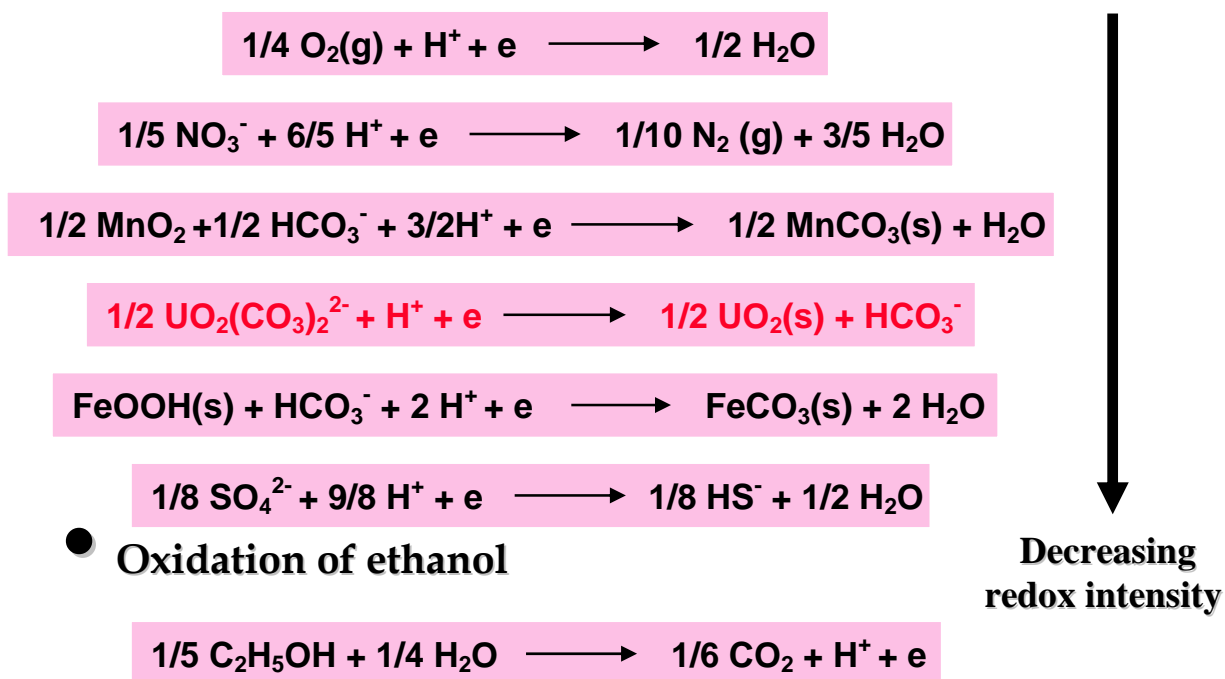
$$1/4 \, O_2(g) + H^+ + e \longrightarrow 1/2 \, H_2O$$

$$1/5 \, NO_3^- + 6/5 \, H^+ + e \longrightarrow 1/10 \, N_2 \, (g) + 3/5 \, H_2O$$

$$1/2 \, MnO_2 + 1/2 \, HCO_3^- + 3/2 H^+ + e \longrightarrow 1/2 \, MnCO_3(s) + H_2O$$

$$1/2 \, UO_2(CO_3)_2{}^{2-} + H^+ + e \longrightarrow 1/2 \, UO_2(s) + HCO_3^-$$

$$FeOOH(s) + HCO_3^- + 2 \, H^+ + e \longrightarrow FeCO_3(s) + 2 \, H_2O$$

$$1/8 \, SO_4{}^{2-} + 9/8 \, H^+ + e \longrightarrow 1/8 \, HS^- + 1/2 \, H_2O$$

Decreasing redox intensity

● **Oxidation of ethanol**

$$1/5 \, C_2H_5OH + 1/4 \, H_2O \longrightarrow 1/6 \, CO_2 + H^+ + e$$

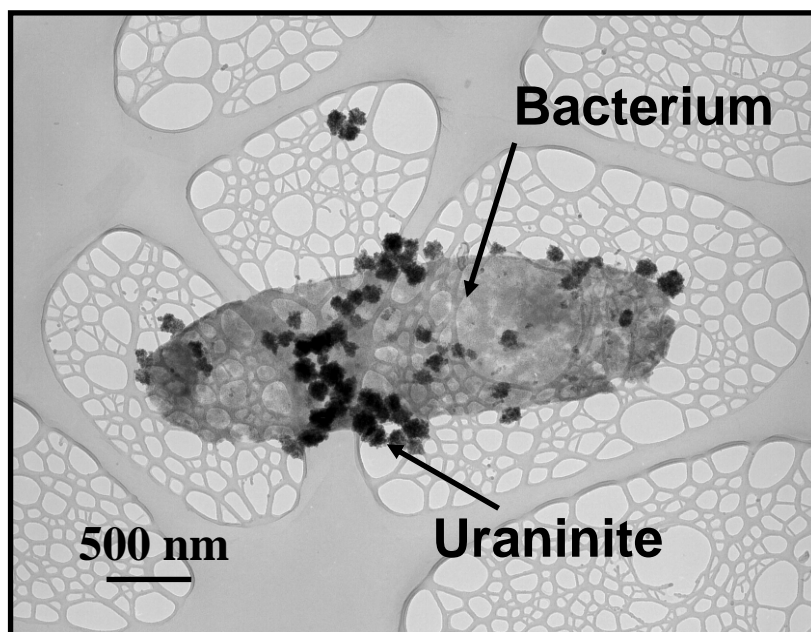**Figure 17. Reductive and oxidative reactions**

Figure 18. Microphotographs showing a bacterium surrounded with uraninite nanoparticles

The first demonstration of a feasible process for the in-situ immobilization of uranium as a bioremediation strategy was conducted by a team of scientists from the University of Massachusetts, PNNL, the University of Tennessee, and several other institutions (Anderson 2003). The team conducted a two-month field study and demonstrated that by adding acetate to the subsurface, they could stimulate the growth and proportion of *Geobacter* species within the subsurface microbial community. At the same time, the concentration of uranium in the ground water was greatly reduced.

The observation of bacteria able to immobilize uranium is an area of active study, both from biochemical and nano-geological perspectives. Comparatively little is known about either the bacteria or the processes they use; even questions over the long-term stability of the immobilized uranium have yet to achieve a comprehensive answer. Recent research at Virginia Polytechnic Institute (Virginia Tech 2006) with *Shewanella oneidensis* MR-1 (one of the most common bacteria in the Earth) has shown that particle size is important, with smaller nanoparticles of the iron (III) oxide hematitie showing a lower rate of reduction than larger nanoparticles. Research on the same bacterium at PNNL (Marshall 2006) has demonstrated that much of *Shewanella*'s biochemistry of immobilization occurs outside the cell, producing uniform, 5-nm particles of uraninite trapped as strings of particles in a glue-like extracellular polymeric substance (Figure 19).
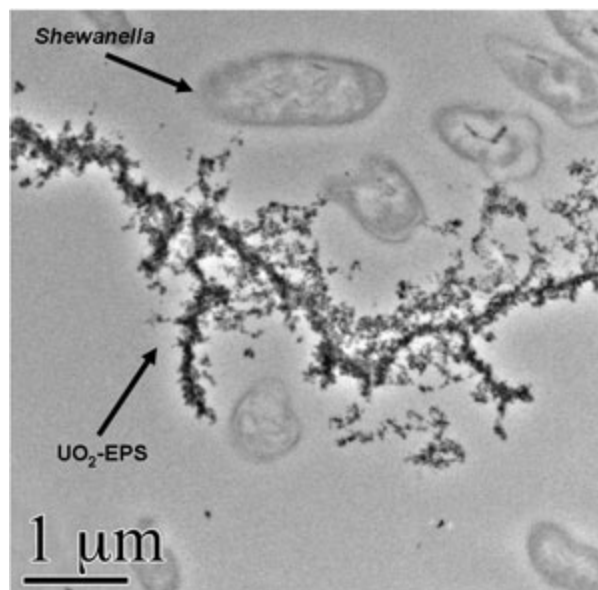

Figure 19. Uraninite nanoparticles trapped in an extracellular polymeric substance exuded by *Shewanella*

A current five-year, $15-million U.S. Department of Energy (DOE) project led by Oak Ridge National Laboratory (ORNL) (Edwards 2007) is trying to provide a further understanding of the coupled microbiological and geochemical processes limiting radionuclide bioremediation, and through an examination of terminal-electron accepting processes involving *geobacteraceae* has shown that due to the stress imposed by low pH on microbial metabolism, the terminal-electron accepting processes of acidic subsurface sediment are inherently different from those of neutral pH environments and

neutralization will be necessary to achieve sufficient metabolic rates for radionuclide remediation.

In addition to direct bacterial processes for the reduction of uranium, indirect processes may occur where bacteria or other microbes assist in the reduction processes by control of the chemical environment. The dissimilatory iron reducing bacteria mentioned above metabolically couple the oxidation of organic compounds with the reduction of Fe (III) generating energy and Fe(II) complexes, the latter of which in turn lead to the production of a range of Fe(II) minerals such as magnetite, siderite, vivianite, ferruginous smectite, and green rust. In fact, the oxidation/reduction behavior of uranium, together with the ability of micro-organisms to take advantage of such oxidation/reduction behavior, may well play a significant role in the formation of uranium ore deposits (Dexter-Dyer 1984). This behavior is being exploited in the concept of microbial mining of uranium, and may be of importance to remediation. An example is "green rust", a class of iron (II)/iron (III) hydroxide compounds having a pyroaurite-type structure consisting of alternating positively charged hydroxide layers and hydrated anion layers. Green rusts are products of both abiotic and microbially induced corrosion of iron, and occur in both microbially mediated and abiotic reductive dissolution of ferric oxyhydroxides. Extended X-Ray Absorption Fine Structure (EXAFS) studies have shown that uranyl ion can be reduced to UO_2 (U(IV)) by green rust (O'Loughlin 2003), with the uraninite forming nanoparticles on the green rust crystal surface (Figure 20).
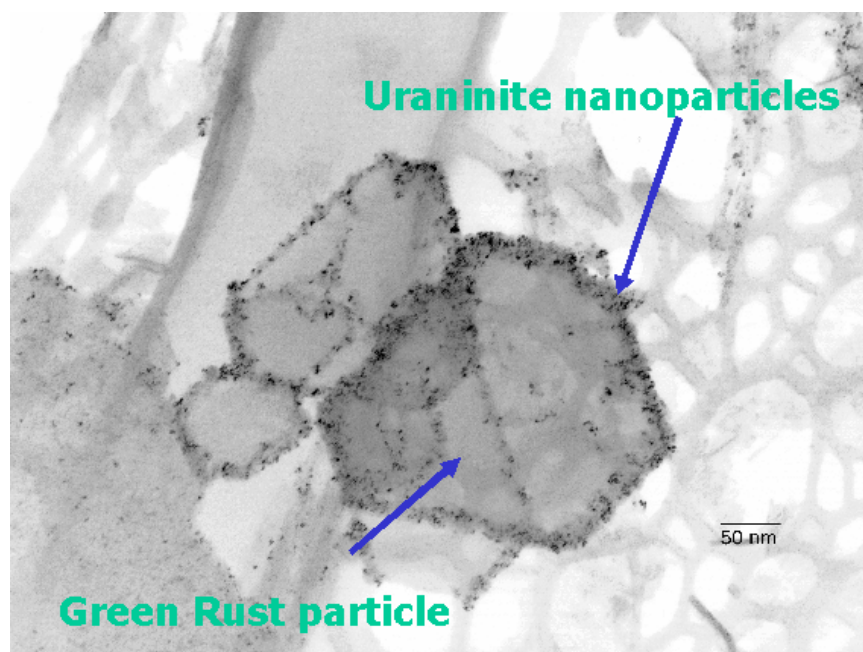
**Figure 20. Uraninite nanoparticles on a green rust particle**

The DOE has funded a project through its Environmental Management Science Program (EMSP) to examine the processes underlying the potential use of dissimilatory metal-reducing bacteria (DMRB) to create subsurface redox barriers for immobilizing uranium

and other redox-sensitive metal/radionuclide contaminants (Roden 2005). The results of these studies suggest that:

- the efficiency of dissolved U(VI) scavenging may be influenced by the kinetics of enzymatic U(VI) reduction in systems with relative short fluid residence times;
- association of U(VI) with diverse surface sites in natural soils and sediments has the potential to limit the rate and extent of microbial U(VI) reduction, and in turn modulate the effectiveness of in-situ U(VI) bioremediation; and
- abiotic, ferrous iron (Fe(II))-driven U(VI) reduction is likely to be less efficient in natural soils and sediments than would be inferred from studies with synthetic Fe(III) oxides.

A key implication of these findings is that production of Fe(II)-enriched sediments during one-time (or periodic) stimulation of DMRB activity is not likely to permit efficient, long-term abiotic conversion of U(VI) to U(IV) in biogenic redox barriers designed to prevent far-field subsurface U(VI) migration. Instead, ongoing DMRB activity will be required to achieve maximal U(VI) reduction efficiency.

The study of dissimilatory metal reducing bacteria (DMRB, the general class of which dissimilatory iron reducing bacteria are part) has recently led to some interesting nanoscience discoveries that may offer new directions for nanotechnology. While most biological oxidation-reduction reactions take place in the liquid phase using water soluble species, dissimilatory reductions require a process where the electron acceptor is a solid phase material. Understanding the details of this process has been the topic of much research, with the focus largely being on c-type (monomeric) cyctochromes (heme proteins generally bound in cell membranes) which are known to perform electron transport. In 2005, Derek Lovley, who discovered *Geobacter* in 1987, published research showing that conductive structures (known as pili or "microbial nanowires") only a few nanometers wide but microns long, are produced by *Geobacter*, are electrically conductive, and are indicated as being involved in electron transport (Reguera 2005). Subsequently, an international group (Gorby 2006) showed that other bacteria can be induced to produce nanowires (as small as 10 nm in diameter, but can reach hundreds of microns in length) when kept in an oxygen-starved state, are electrically conductive, and that this behavior is not limited to DMRB but might be a common bacterial strategy for efficient electron transfer and energy distribution. When in a community, the bacterial nanowires can cross and touch, and may allow for sharing of electrons among a network of bacteria. Figure 21 illustrates the bacterial nanowire reaching across organisms, and Figure 22 depicts a close-up image of a nanowire. The nanowires have been of great interest as a potential production and supply method of nanowires for other applications (such as sensors, nano-electronic components), as the basis of a possible remedial treatment approach, or as a component of microbial fuel cells.
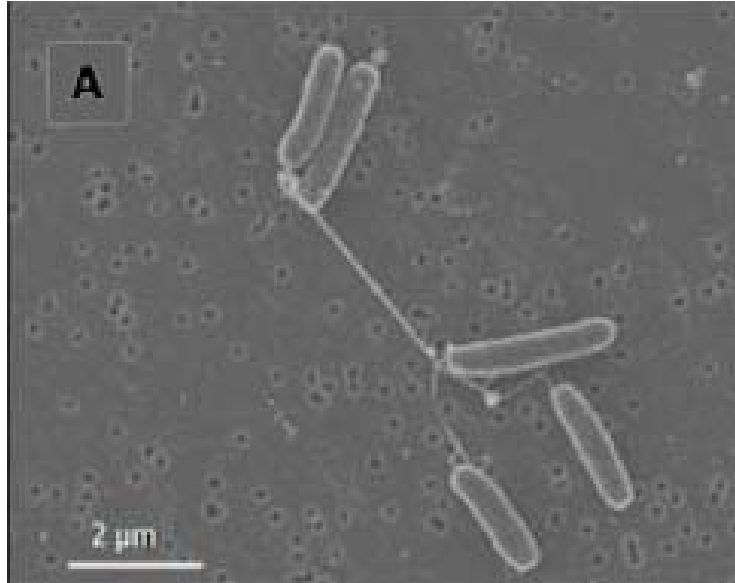
Figure 21. Scanning electron microscope image of
Shewanella ddeinensis **strain MR-1**
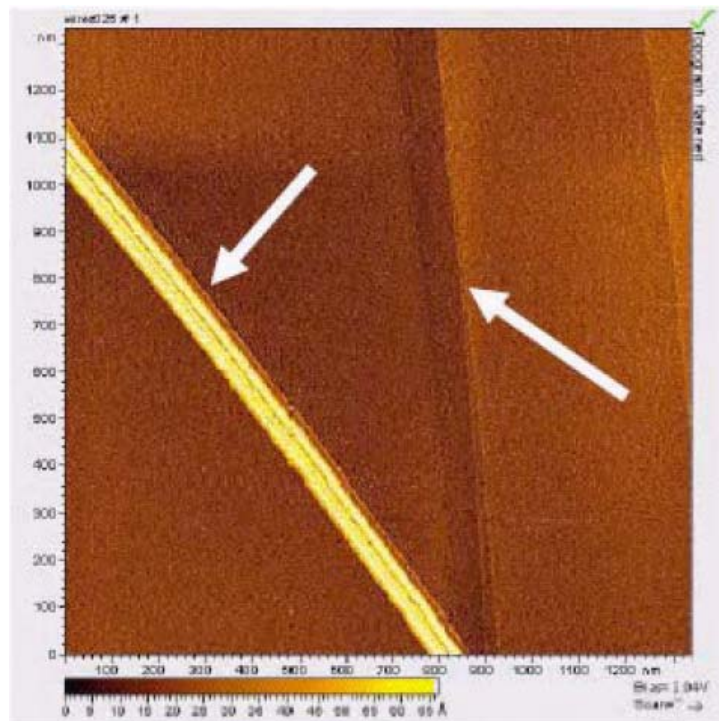
Figure 22. Scanning Tunneling Microscope (STM) images of isolated nanowires from wild-type MR-1, with lateral diameter of 100 nm and a topographic height of between 5 and 10 nm. Arrows indicate the location of a nanowire and a step on the graphite

In summary, the literature on microbially mediated reduction of U(VI) showed that U(VI) can be reduced to U(IV) by enzymatic activity of microorganisms, including:

- metal- and sulfate-reducing bacteria;
- U(VI) can be reduced either by pure cultures or by mixed indigenous cultures;
- U(IV) precipitates as uraninite (UO_2);
- complexation of U(VI) with organic and inorganic ligands can inhibit its reduction by microorganisms; and
- complexation of U(IV) may inhibit its precipitation.

Uranium reduction by bacteria is an example of bioremediation. As its advocates point out, bioremediation may be regarded as the oldest environmental technology of all, having existed virtually as long as the human species. Prior to 1989, bioremediation as a formal environmental technology was not widely known; it had a small number of advocates, though its claims were backed by considerable laboratory and academic work. The March 1989 Exxon Valdez disaster in Alaska and the subsequent use of bioremediation using naturally occurring marine organisms together with added nutrients, opened the way for bioremediation to become an established environmental remediation option. Economically, bioremediation usually offers great overall cost savings compared to competing technologies. In addition, risks tend to be smaller since contaminants are not transferred from one medium to another for processing, and there is no waste transportation involved. On the other hand, the bioremediation process may take much longer than chemical or physical treatment alternatives, requiring ongoing monitoring to ensure that progress is being made. When geological conditions are suitable and sufficient time is available, bacterial reduction of uranium is likely to be an attractive remedial alternative.

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